VARIABILITY IN THE INHERENT OPTICAL PROPERTIES FOR THE NORTHEASTERN GULF OF MEXICO: APPLICATION TO A SEMI-ANALYTICAL OCEAN COLOR ALGORITHM

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ABSTRACT

Chlorophyll *a* concentrations in the Northeastern Gulf of Mexico during an August 1997 cruise spanned nearly two orders of magnitude ranging from 0.13 mg m^{-3} to 4.3 mg m^{-3}. High Performance Liquid Chromatography (HPLC) data indicates a taxonomic shift from cyanophytes, prochlorophytes, and prymnesiophytes dominating the offshore stations to diatoms and the Florida red tide species Gymnodinium breve dominating the nearshore stations. This shift is accompanied by changes in pigment packaging due to variations in size and internal pigment concentrations along with differences in accessory pigment types and concentrations. A semi-analytic algorithm yielded a 27% root mean square error when predicting chlorophyll *a* concentration for offshore stations and a 76% RMS error for nearshore stations dominated by large-celled phytoplankton populations. Understanding regional changes in absorption properties in order to implement the appropriate parameters is critical for increasing the accuracy of remote-sensing algorithms to derive ocean color constituents.

INTRODUCTION

Satellite remote-sensing of ocean color is a rapidly developing field as scientists understand more about the various constituents that produce the ocean's color. Additional visible wavebands on current and future ocean color sensors (i.e. SeaWiFS, MODIS, etc.) will allow for more information about these color constituents to be teased out using various algorithms. Case 1 oceanic waters in which chlorophyll covaries with colored dissolved organic matter (CDOM) and detritus are fairly well understood. Simple two band algorithms utilizing the $R_{rs}(440)/R_{rs}(550)$ ratio have proven effective at estimating chlorophyll *a* concentration in such waters (Gordon ,1983). Case 2 waters, however, pose several difficulties when attempting to calculate chlorophyll *a* from remote-sensing reflectance (Carder ,1991). Optical constituents including CDOM and detrital absorption no longer covary with algal biomass in Case 2 waters. Also, phytoplankton absorption spectra are subject to variability in accessory pigment composition due to changes in taxonomy or to adaptation to different light and nutrient regimes (Hoepffner ,1991). Absorption properties of phytoplankton are also sensitive to the pigment package effect. Simply put, larger more heavily pigmented cells absorb light less efficiently than their smaller less pigmented counterparts.

Coastal environments have recently gained the attention of oceanographers concerned with applications including mapping river plumes, monitoring toxic algal blooms, calculating DOC budgets, etc. A semi-analytic algorithm has been introduced by Carder et. al. (1998) for calculating the optical constituents of seawater (i.e. chlorophyll *a* and CDOM absorption) in Case 1 and Case 2 environments taking into consideration the complications mentioned above. Three sets of parameters (unpackaged, global, and packaged) for modeling the various optical components have been generated in order to improve algorithm performance for different regions and seasons. In this paper, data collected in August 1997 from the West Florida Shelf are tested using this semi-analytic algorithm. The results are discussed in terms of phytoplankton taxonomy, size, and pigmentation along with the relative contributions that absorption due to CDOM has on total absorption.

METHODS

Surface samples were collected using Niskin bottles attached to a rosette sampler aboard the R/V Anderson during August, 1997. An hourglass-shaped set of transect lines was followed between Tampa Bay and Charlotte Harbor. An additional 49 samples from a grid of stations were collected in the Northern Gulf of Mexico. The rosette was geared with a Sea-Bird SBE 9 CTD that was deployed at each station. Phytoplankton absorption spectra ($a_{ph}(\lambda)$) and remote-sensing reflectance spectra ($R_{rs}(\lambda)$) were measured at 15 hourglass and 15 Northern Gulf stations using a 512-channel spectral radiometer (Lee ,1996; Bissett ,1997). Chlorophyll *a* and pheopigment concentrations were measured fluorometrically with a Turner 10-AU-005 fluorometer. Frozen filter samples were processed by HPLC (Wright ,1991). Particle size distributions were measured using a Multisizer II Coulter Counter. Principal Component Analysis was made using the Statistical Analysis System (SAS).

RESULTS

Hydrography

The hourglass transect region features a relatively high temperature, high salinity (36ppt) water mass just offshore of the west coast of Florida that is adjacent to a lower temperature, lower salinity (33.75ppt) mass of water further to the west (Figures 1a,c). Chlorophyll *a* concentrations decrease steadily with movement offshore. The low salinity water mass exhibits chlorophyll *a* concentrations slightly higher than in surrounding regions (Figure 1e).

The set of 49 stations in the Northern Gulf exhibit a plume of fresher water that extends from west to east in the center of the grid (Figure 1d). Surface temperatures increase steadily offshore (Figure 1b). The high salinity, high temperature region south of the fresher water has elevated chlorophyll *a* concentrations greater than 2 mg m^{-3}.

Stations within the freshwater plume exhibit lower chlorophyll *a* concentrations less than 2 mg m^{-3} (Figure 1f).

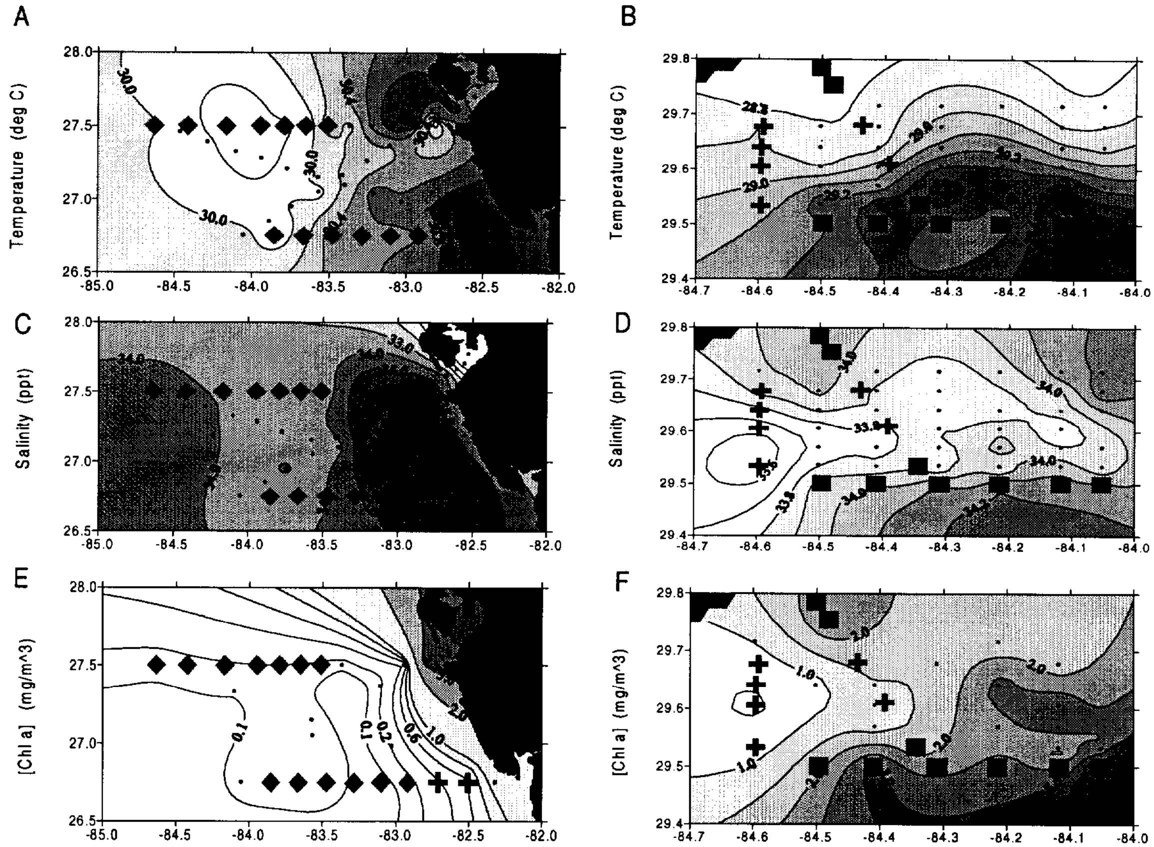

***Figure 1**: Contour plots of surface temperature, salinity, and chlorophyll* a *concentration for the hourglass transects (a,c,e) and the Northern Gulf of Mexico (b,d,f). Group 1 (diamonds), Group 2 (crosses), Group 3 (boxes); Contour data points (small circles)*

Taxonomy: Pigmentation and Cell Size

Surface stations in the Gulf of Mexico were divided into three groups based on HPLC pigment signatures using Principal Component Analysis (PCA). This statistical tool reduces multiple variables into a few manageable principal components to summarize the data trends. The first two components in this data set explain 69% of the standardized variance and the first three components explain 83% of the standardized variance. The relative accessory pigment compositions for these three groups can be examined in Figure 2. Group 1 stations located west of the 30m isobath in the hourglass region are composed mainly of prochlorophytes (chl a_2), cyanophytes (zeaxanthin), and prymnesiophytes (19'hexanoyloxyfucoxanthin). The non-photosynthetic or photoprotective carotenoids zeaxanthin and diadinoxanthin together make up 37% of the total accessory pigment concentration. Particles for these stations are mostly less than 10μm in diameter (Figure 3d).

In contrast, Group 3 stations located in the high salinity, high temperature waters in the Northern Gulf are composed mostly of diatoms and the toxic bloom-forming dinoflagellate Gymnodinium breve common to the Gulf of Mexico. Photosynthetic accessory pigments typical of G. breve are the 19'acylofucoxanthins, fucoxanthin, chl c_{1+2+3} ,and the taxon-specific marker carotenoid gyroxanthin-diester (Millie ,1995). G. breve cells were found at maximum concentrations of 280,000 cells liter^{-1} in this region.

These cells appear as an 18μm peak in the coulter counter particle size distributions. Diatoms may be responsible for the 11μm peak (Figure 3d).

Two stations belonging to Group 2 are located offshore Charlotte Harbor (26.5°N) and consist of chlorophyll b containing chlorophytes or prasinophytes (lutein/chl a_1=0.11) along with diatoms (fucoxanthin). The remaining Group 2 stations are located in the low salinity plume waters of the Northern Gulf along the western edge of the grid and also at 29.5 °N, 84.3°W – a location occupied for ~30 hours and sampled periodically. These stations were composed of a mixture of diatoms (fucoxanthin), cyanophytes (zeaxanthin), prochlorophytes (chl a_2), and some G. breve. The average particle size distribution for Group 2 stations is similar to that of Group 3 stations except for the absence of a 10μm peak and the presence of an 18μm peak that is about half the size.

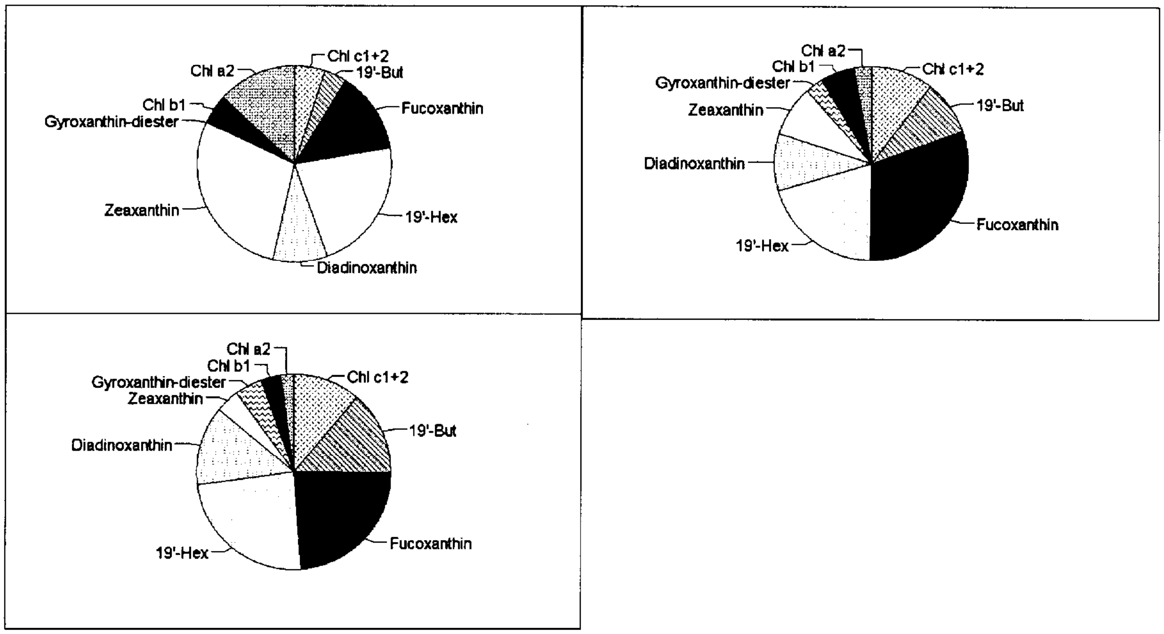

Figure 2: *Relative accessory pigment contributions for Group 1 (upper left), Group 2 (upper right), and Group 3 (lower left).*

Optical Properties

Optically, the magnitude of the average phytoplankton absorption spectra (Figure 3a) differs significantly between the three groups of stations as does the shape of the specific absorption spectra (Fig 3b). Group 3 stations, with chlorophyll *a* concentrations greater than 1 mg m^{-3} exhibit high overall absorption and a low $a_{ph}^*(432)$~0.045 m^2 mg^{-1}. Conversely, Group 1 stations with chlorophyll *a* concentrations less than 0.25 mg m^{-3} exhibit low absorption values and a high $a_{ph}^*(432)$~0.08 m^2 mg^{-1}. At 443nm, CDOM absorption typically is equal to or greater than phytoplankton absorption up to a factor of 3:1. Stations with high $a_g(443)/a_{ph}(443)$ ratios in both freshwater plumes of the hourglass region and the Northern Gulf have slightly enhanced $a_{ph}(545)$ shoulders most likely due to phycoerythrin pigments belonging to cyanophytes.

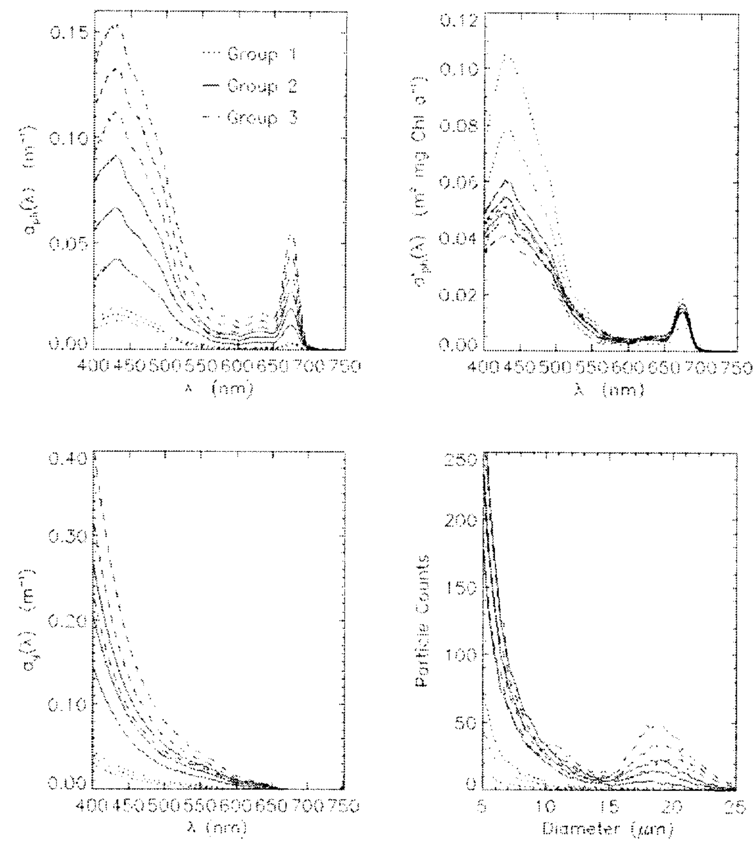

***Figure 3**: A) Phytoplankton absorption spectra, B) Chlorophyll* a *specific absorption spectra, C) CDOM absorption spectra, D) Particle size distributions. Lines represent means +/- 1 SD.*

Algorithm Results

The semi-analytic algorithm (Carder ,1998) yields a root mean square error of non-log transformed chlorophyll *a* measured versus modeled values of 43% (n=36) if all stations are processed together using unpackaged parameters. This error drops to 27% (n=11) if Group 1 stations are considered separately and to 17% if an $a^*_{ph}(675)=0.015\ m^2\ mg^{-1}$ is applied. Group 2 stations exhibit larger RMS errors of 48% (n=12) using the unpackaged parameters and 32% using the packaged parameters. Group 3 stations yield even larger RMS errors of 76% (n=7) using the unpackaged parameters and 48% using the packaged parameters.

Discussion

August in the Gulf of Mexico is a time when irradiance levels are generally high and surface nutrient concentrations low. Consequently, phytoplankton populations are expected to be both small as they rely on recycled nutrients and high-light adapted (i.e.

low intracellular pigment concentrations). This generalization, however, does not apply to nearshore waters exposed to additional nutrient sources (i.e. riverine systems and bottom resuspension) and to light limitation due to high CDOM absorption. In this study, stations close to land belonging to Groups 2 and 3 yield high RMS errors (48% and 76%, respectively) when applying unpackaged parameters in a semi-analytic algorithm. Offshore Group 1 stations perform better in the algorithm (RMS=27%) as expected. Stations dominated by G.breve perform poorly most likely due to their large size (18μm) and high accessory pigment concentrations. Such factors would exaggerate the pigment package effect.

Regional parameters must be applied in coastal environments in order to maximize performance of the semi-analytic algorithm (Carder, 1998). In this study, stations that yielded high RMS errors are located in high temperature, high salinity regions of both the Northern Gulf of Mexico and the hourglass transects. Whether this observation can be utilized as a means of partitioning unpackaged from packaged stations in coastal environments via a sea surface temperature observing satellite (AVHRR) is a subject that will be further explored.

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